Interfacial phase transitions at solid/fluid and liquid/vapour interfaces

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ABSTRACT

To study the interface between a solid surface and nitrogen vapour, the theory of Cahn was applied. For that purpose the Peng-Robinson equation of state (PREOS) was incorporated in the theory of Cahn to model the thermodynamic functions of the fluid. In this study the wetting transition, as earlier reported by Cahn, was shown. In addition, wetting transitions occurring at a liquid-vapour interface of the three-phase LLV equilibrium of the binary mixtures hexane/water and benzene/water were examined. It was found that by making use of the gradient theory of van der Waals, in which the PREOS was incorporated, the transitions seem to be of third order. In case the PREOS was replaced by the Associated-Perturbed-Anisotropic-Chain-Theory, no wetting region was found. It was argued that, in principle, it should be possible to model first order wetting transitions with the square gradient theory.

KEY WORDS: Cahn theory; equation of state; fluid mixtures; interfacial tension; pure fluids; square gradient theory; wetting transition.

1. INTRODUCTION

In recent publications it has been shown that interfacial tension effects can strongly influence the recovery efficiencies during the process of enhanced oil recovery [1,2]. In such cases it is extremely useful to know the interfacial tension behaviour in the reservoir, and how it can be influenced. In the same context it is believed that the phase transitions that occur at solid surfaces or at oil/water interfaces play a role during the recovery. In the present paper these transitions will be examined. The most important aspect is that wetting of an interface can occur at (or close to) the state of three-phase equilibrium and that at such a state of wetting the three interfacial tensions between the bulkphases A, B, and C, denoted as γ_{AB} , γ_{AC} , and γ_{BC} , are interrelated via:

$$\gamma_{AB} = \gamma_{AC} + \gamma_{BC} \tag{1}$$

In case we are in a situation of partial wetting, the three interfacial tensions satisfy the inequality of Neumann [3]:

$$\gamma_{AB} < \gamma_{AC} + \gamma_{BC}$$
 , $\gamma_{AC} < \gamma_{AB} + \gamma_{BC}$, $\gamma_{BC} < \gamma_{AB} + \gamma_{AC}$ (2)

It has been observed experimentally [4, 5, 6] that partial-wetting occurs along the triple line up to a certain point where the interface becomes wetted. It is this transition that will be studied in the present contribution. Above the wetting temperature there exists a macroscopic thick layer of phase C in the AB interface. Continuity suggests that near a three-phase coexistence there should also be a thick layer with a composition close to that of C at the AB interface. The thickness of this layer is expected to diverge if the three-phase equilibrium is approached. For a more extensive description of wetting transitions one is referred to elsewhere [7,8].

In this paper section 2 summarizes very briefly the theory applied to describe the behaviour of fluids near solid surfaces and for the study of fluid interfaces. Section 3.1 shows the wetting transition for a vapour in contact with a solid surface, and section 3.2 shows the wetting transitions that occur at water/hexane and water/benzene interfaces. The theory applied in this section is the square gradient theory of van der Waals [9], in which a suitable equation of state is incorporated.

2. THEORY

In addition to the just mentioned wetting transitions pre-wetting transition can occur at fluid-solid interfaces, i.e., the so-called Cahn-transition. To enlighten this behaviour, the original theory of Cahn [10] is used. Because the theory is described extensively in the paper of Cahn, only the basic equations will be presented here. The interfacial tension of a pure fluid in contact with a solid wall can be written as:

$$\gamma = \Psi(\rho_s) + 2 \int_{\rho_0}^{\rho_s} \sqrt{c \, \Delta\omega(\rho)} \, d\rho \qquad (3)$$

, where ρ_0 is $\rho(x=\infty)$ the equilibrium bulk density and ρ_s is the density at the solid wall. $\Psi(\rho_s)$ is a function of density and is specified in the following section. In Eq. (3) the term $\Delta\omega(\rho)$ arises from the gradient term present in Cahn's theory and is defined as $f(\rho)-\mu_0\rho+p_0$, where $f(\rho)$ is the Helmholtz free energy density obtained from the PREOS, μ_0 is the equilibrium chemical potential, and $-p_0$ is the equilibrium pressure.

For the description of the behaviour of fluid interfaces at three-phase equilibrium, the square gradient approach of van der Waals [9] is applied. The interfacial tension of a planar interface can be expressed in this theory as:

$$\gamma = \int \left[f(\boldsymbol{\rho}) + \sum_{i,j=1} c_{i,j} \nabla \rho_i \cdot \nabla \rho_j - \sum_{i=1} \mu_{i_0} \rho_i + p_0 \right] dx$$
(4)

, where the index 0 indicates thermodynamic equilibrium, ∇ represents d/dx, and c_{ij} is the so-called influence parameter, which, in principle, can be a function of density and temperature, but is kept constant in the present contribution. In this study the Helmholtz free energy density, $f(\rho)$, is modelled using the Peng-Robinson [11] equation of state (PREOS) or Associated-Perturbed-Anisotropic-Chain-Theory (APACT) developed by Donohue and coworkers [12,13]. This latter theory incorporates the effect of hydrogen bonding, anisotropic interactions on top of isotropic interactions. Therefore, it is believed that this theory will be more suitable for the thermodynamic description of water containing mixtures, as is the case in the present study.

3. RESULTS

3.1. Wetting transitions at solid/vapour interfaces

In the present section the wetting transitions are shown that are encountered for a vapour in contact with a solid surface. Therefore the interfacial tensions for nitrogen vapour in contact with a solid surface are computed according to the theory of Cahn [10]. It is assumed that $\Psi(\rho_s)$ is a linear function of density: $\Psi(\rho_s)=(\rho_s-\rho_0)\cdot 10^{-7}+20$ (mN/m), where densities are to be expressed in mol/m³. This function has no experimental background, but for the purpose of the present discussion it suffices. The influence parameter, c, equals 0.886 10^{-20} J/m⁵mol² [14] and the coexisting phases of nitrogen have been modelled using the PREOS. In the theory of Cahn three different densities of contact at the solid surface can be obtained and thus three different interfaces can be constructed. The interfacial tensions of the three interfaces along nitrogen's liquid-vapour coexistence curve are plotted in Fig.

1, which shows that the interface represented as the dotted line has always a larger interfacial tension, compared to the other two. Therefore, this interface will never be encountered in practice. At temperatures below 110 K the interfacial tension represented with the solid line has a lower value than the tension represented with the dot-dashed line, i.e., the solid line represents the actual interfacial tension and appears to be associated with the non-wetted interface. Above 110 K the interfacial tension denoted with the dot-dashed curve will be the actual one, i.e., the wetted interface is stable. Thus at 110 K the wetting transition takes place and is of first order. Another striking aspect of Fig. 1 is that the interfacial tension in the wetted region shows a minimum. Whether this has been observed experimentally is not known. The pre-wetting line has been computed for this system as well. It was shown [14,15] that this line is located very close to the vapour side of the coexistence curve, which is in agreement with experimental observations [4,5].

3.2. Wetting of fluid interfaces

For the present study of the wetting transitions at fluid interfaces, two binary mixtures will be studied, namely, the system hexane/water and benzene/water. In both systems computations are performed with the PREOS and the APACT model in conjunction with the gradient theory. For a complete description of the gradient theory and its connection to modern semi-empirical equations of state, one is referred to elsewhere [14,16]. All parameters used for this set of calculations have been taken from Cornelisse [14]. The influence parameters, c_{ij} , for the studied systems are given in Table I. The value of the influence parameter c_{ij} of the unlike species are computed from $c_{ij}=(1-c_{ij})(c_{ii}c_{jj})^{1/2}$, where the mixing parameter c_{ij} is an adjustable parameter [14,15].

The binary mixture composed of water and hexane shows a three-phase equilibrium

line of type-III fluid phase behaviour in the classification of van Konijnenburg and Scott [17] with hetero-azeotropy. The phase diagrams computed with the PREOS and APACT have been presented elsewhere [14,15]. After evaluation of the phase equilibria, the interfacial tensions can be calculated. The results are shown in Fig. 2. In this figure the solid lines represent the computed interfacial tensions obtained with the APACT model for the three interfaces that can formed at three-phase equilibrium, while dashed lines represent the results obtained with the PREOS.

It is striking that the agreement between theory and experiment is excellent for the APACT model. The PREOS performs not as good as the APACT model but is still capable to approach the experimental values. The dot-dashed lines denote the summation of the GL1 and L1L2 interfacial tensions that becomes important in the discussion on wetting transitions. It is clear from Fig. 2 that at low temperatures this line (for both PREOS and APACT) is located just above the line of the tension of the GL2 interface, and thus the interfacial tensions satisfy Neumann's inequality (Eq. 2).

At higher temperatures it can be seen in Fig. 2 that for the PREOS the tension of the GL2 interface becomes gradually equal to that of the sum of the GL1 and the L1L2 interfaces, reflecting the fact that the interface becomes wetted. It is clear that in the GL2 interface a layer of the second liquid phase of composition L1 intrudes between the G and the L2 phase, which yields a tension for the GL2 interface that is exactly equal to the summation of the interfacial tension of the GL1 and the L1L2 interfaces. For the APACT model never a wetting transition occurs, which is reflected as well in the density profiles computed with the APACT model [14,15]. Whether this behaviour has been observed experimentally is not known.

Similar observations have been encountered for the binary system composed of

water and benzene and thus no wetting transition has been obtained by making use of APACT. Therefore, it was decided to examine only the results obtained from the PREOS. For a complete discussion on the description of the phase behaviour by means of the PREOS, we refer to elsewhere [14,15]. The most important observation from this discussion is that the PREOS erroneously predicts an azeotrope from about 543.15 K to 568.15 K and an LL critical endpoint of the three-phase line, while a GL1 critical endpoint has been observed experimentally [18]. However, for examination of a wetting transition without making comparison with experiments, these differences become irrelevant. Subsequently, the interfacial tensions are presented in Fig. 3. The parameter used for this graph amounts 1.0 [14]. This graph clearly shows that again a wetting transition occurs along the three-phase line, as was observed already in the system water/hexane.

The point where the wetting transition occurs is hard to determine in the present graph. Therefore, it was decided to take the derivatives of the interfacial tension with respect to temperature. The first derivative shows a smooth curve and is not presented here. Fig. 4 represents the second derivative of the GL2 interfacial tension and the second derivative of the sum of the interfacial tensions of the GL1 and L1L2 interfaces. From Fig. 4 it becomes apparent that the wetting transition takes place at a temperature equal to 510 K, while the figure seems to indicate as well that the wetting transition predicted by the PREOS in conjunction with the gradient theory is of third order.

Whether a wetting transition obtained by means of the gradient theory should always be of higher order cannot be completely resolved here, but there are two aspects that point into another direction. The first originates from computations obtained with the APACT in conjunction with the gradient theory. It can be concluded from these computations that three non-wetted interfaces can be obtained, even very close to the critical endpoint of the

three-phase line. If this is true, than a first order transition might be found as well, that is, when at a certain temperature the summation of the GL1 and the L1L2 interfacial tension becomes less than the tension of the GL2 interface. However, for the systems under study no such a transition was found. The second aspect that makes it hard to believe that no first order transitions can be found by means of the gradient theory originates from the study of a model used by Szleifer and Widom [19]. With this model it appeared to be possible to obtain first order transitions. For a more extensive discussion on this matter we refer again to elsewhere [14,15].

4. CONCLUSIONS

In a study for a pure saturated vapour (nitrogen) in contact with a solid surface, using the Cahn theory in conjunction with the PREOS, it has been shown that with such a simple model a wetting transition can be obtained. This transition is the well known Cahnwetting transition being of first order.

From studies of interfacial tensions at the state of three-phase liquid-liquid-vapour equilibrium in a binary mixture, it was found that the gradient theory in conjunction with a proper equation of state (APACT), can provide an accurate description of the interfacial tensions at lower temperatures (system water/hexane). In addition, a study is presented on the nature of wetting transitions all long the three-phase line present in the binary systems water/benzene and water/hexane (type-III fluid phase behaviour with hetero-azeotropy). It appeared that the PREOS with the gradient theory for both systems seems to predict a wetting transition of third order. On the other hand, with the APACT equation never a wetting transition could be obtained. It has been argued in section 3.2 that it might be possible, in principle, to obtain a first order wetting transition from the gradient theory

depending on the morphology of the free-energy density surface.

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Table I. The influence parameters used in the gradient theory

	c_{ii} for PREOS	c_{ii} for APACT model
	$10^{-20} \text{ J/m}^5 \text{mol}^2$	$10^{-20} \text{ J/m}^5 \text{mol}^2$
hexane	42.67	37.08
benzene	25.40	24.10
water	1.384	1.066

FIGURE CAPTIONS

- Fig. 1. The solid/vapour interfacial tensions computed from the Cahn theory in conjunction with the PREOS along the liquid-vapour coexistence curve of nitrogen. The three lines denote the interfacial tension for the three different densities of contact at the solid surface. Fig. 2. Interfacial tensions at three-phase equilibrium. Solid lines APACT with $_{ij}$ =0.53; dashed lines PREOS with $_{ij}$ =0.48; dot-dashed lines summation of GL1 and L1L2 tensions (line labelled A=APACT, line labelled P=PREOS); solid circles experiments [20].
- Fig. 3. Interfacial tensions at three-phase equilibrium in system water/benzene. Solid lines PREOS with _{ij}=1.0; dashed lines summation of GL1 and L1L2 tensions.
- Fig. 4. Second derivative of the GL2 tension at three-phase equilibrium and of the summation of GL1 and L1L2 tensions in the system water/benzene.

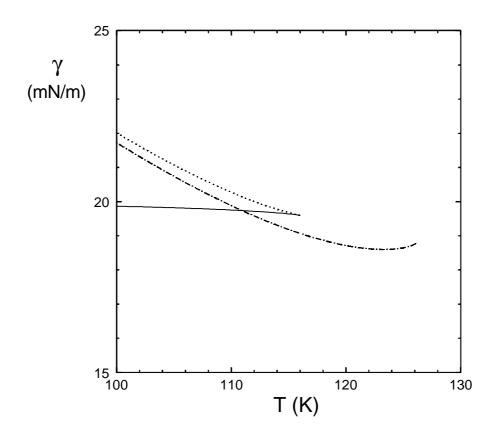


Figure 1. P.M.W. Cornelisse, C.J. Peters, and J. de Swaan Arons.

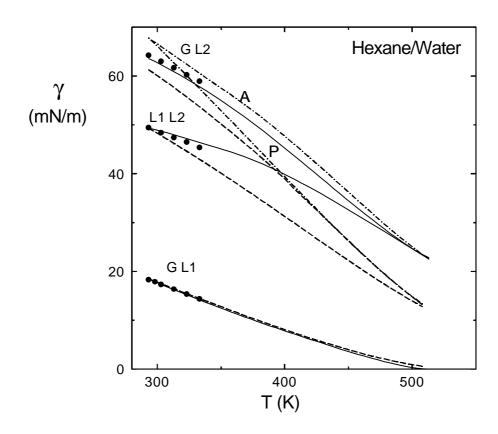


Figure 2. P.M.W. Cornelisse, C.J. Peters, and J. de Swaan Arons

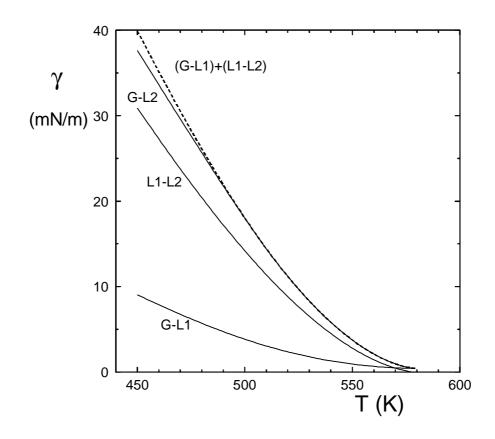


Figure 3. P.M.W. Cornelisse, C.J. Peters, and J.de Swaan Arons.

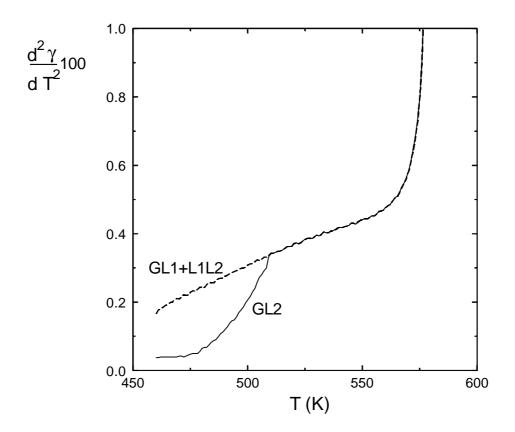


Figure 4. P.M.W. Cornelisse, C.J. Peters, and J. De Swaan Arons.